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COMPLETE SPECIFICATION

Process for the Production of Porous Polyethylene Bodies

We, RUHRCHEMIE AKTIENGESELLSCHAFT, a German company, of Oberhausen-Holten, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to a process for the production of porous polyethylene bodies or masses.

It has been found that porous bodies are obtained when pourings or masses of small particle size, particularly pulverulent, polyethylene having a molecular weight greater than 75000 and preferably greater than 100,000, with or without the simultaneous use of mechanical pressure, are heated to a temperature between 120° C. and that temperature at which, under the pressure employed, decomposition and/or gelation of the polyethylene occurs. Gelation as used in the present specification is to be understood as the formation of structures having a glassy, translucent appearance. The particle size of the polyethylene is preferably below 1 mm. and advantageously below 0.3 mm. Ethylene polymers having molecular weights of more than 75000 and preferably of more than 100,000 can readily be produced by means of suitable polymerisation catalysts at pressures below 200 kg./sq. cm. and at temperatures up to about 100° C.

The shaping or forming of the polyethylene into small particles may be effected in any suitable manner. Apart from pulverulent material, the polyethylene particles may also be used in the form, for example, of granules, fibres, scales, rings, discs, or wire sections, tube sections, sheet sections or small polyhedrons. Mixtures of small particles of different shapes may also be used. For example, granules or scales mixed with fibres or sheet sections may be processed.

It is of particular advantage to use the polyethylene directly in the state in which it is obtained in the polymerisation. This material, however, may also be subjected to a thermal and/or mechanical pre-treatment. In addition to polyethylene of the molecular size mentioned above, the pouring to be treated may contain small particle size or pulverulent highly polymerized materials of a different kind consisting, for example, of polystyrene, polyisobutylene, polyethylene of a molecular weight lower than 75000, and similar materials. Dyes and/or fillers may also be admixed with or in the particulate or pulverulent polyethylene. Examples of fillers which may be used include magnesium carbonate, kieselguhr, calcium carbonate, carbon, titanium white and similar materials suited for the filling of synthetic resins.

The temperatures employed in the process according to the invention and the duration of heating are dependent upon the pressures used and upon the finished products desired. If no external pressure or only a very low mechanical pressure (e.g. a pressure of below 30 grams/sq. cm.) is applied, then the temperatures required lie between 120° C. and about 400° C. It is possible in accordance with the invention to prepare cork-like bodies under different conditions. It is also possible within a certain range of these conditions to obtain bodies which are equal to cork with regard to density porosity, and thermal conductivity. To obtain cork-like bodies, it is necessary to avoid the use of too high pressures in during the heating. It is advantageous to operate without or with only quite moderate pressures as, for example, at 0—50 gms./sq. cm. With polyethylene having molecular weights between 300,000 and 600,000, for example, temperatures ranging between 130° C. and about 170° C. must be applied under these conditions. At temperatures above 170° C., porous bodies are obtained the density of which is higher than that of cork. In general, the hardness of the porous bodies increases as the temperature increases. The mechanical strength of the porous products can readily be increased by continuing the heating for a sufficiently long period of time. The heating may be effected under elevated pressure which

may be produced by mechanical pressing devices, particularly with stamps or pressing plates. A reduction in the volume of the polyethylene will always occur during the treatment in accordance with the invention.

The heating of the pulverulent or particulate polyethylene is preferably effected in the absence of air, for example, *in vacuo*, or in an atmosphere of a gas which is inert to the polyethylene under the conditions of the treatment, for example, nitrogen.

The heating required for the production of porous masses can be effected in any suitable manner. For this purpose, the outside walls of the vessels in which the pulverulent or particulate polyethylene is contained may be provided with tubes or heating jackets through which liquid or gaseous heating media are passed, for example, steam, water under pressure, or organic liquids. The heat may also be supplied by means of hot inert gases or steam which are directly passed through the small particle size pourings being processed.

The use of induction heating is not technically feasible with pulverulent or particulate ethylene polymers because the polymerised hydrocarbons exhibit practically no dielectric loss. When processing pulverulent or small particle size mixtures which, in addition to polyethylene, contain materials having a sufficient dielectric loss, for example, if mixtures of polyethylene and polyvinyl chlorides, polyamides and similar polymers are involved, or when mineral fillers are admixed with the polyethylene, a dielectric heating of the mixtures can be effected. This method of heating has the advantage that pourings of great volume and/or large cross section can be uniformly heated throughout.

The production of the porous masses may also be effected by stage-wise heating. In this case, the small particle size pourings containing ethylene polymers are treated, for example, in two stages with increasing temperatures and, if necessary or desired, different durations of heating.

If the pulverulent or particulate ethylene polymers or polymer mixtures are placed in containers and are heated therein under a slight pressure, then the porous bodies may be given their final shape during production. By using containers of circular or polygonal cross section there may be produced correspondingly profiled rods or strips, particularly cylindrical rods. Porous plates, of rectangular section or of dished form may be produced in flat containers or by means of shelved presses the metallic, intermediate plates of which are brought to the requisite temperature by liquid heat-transfer media. Porous bodies in various other shapes may be produced from pulverulent polyethylene or polyethylene-containing mixtures by means of heatable moulds.

The porous bodies prepared in accordance with the invention can be shaped in various ways by mechanical machining operations, such as by pressing, cutting, stamping, or by cutting operations such as turning, drilling, milling, sawing, planing.

By virtue of their properties, the new porous masses are particularly suitable for many purposes such, for example, as heat insulation, sound absorbers, floating bodies such as lifebelts or life-jackets, various articles or insulating media in the electrical and cable industries and for articles of many other kinds.

It has also been found that porous bodies produced in accordance with the invention can be oxidised superficially with hot air in such a manner as to form a thin layer on the surface which is impermeable to gases and liquids, for example, to water. In this manner shaped bodies of porous polyethylene can be protected against the penetration of gases, vapours or liquids. For this purpose the bodies to be treated are for example, exposed for a short time to a stream of air of a temperature of 170°—200° C. By such a partial oxidation of the surface, the interior of the porous body undergoes no change while the outer surface is rendered impermeable or becomes more impermeable.

For heat insulation purposes, the porous bodies may be used in the form of sheets, dishes, strips or tubes. The porous bodies may also be used in a comminuted state, for example, of the size of peas or nuts, for heat insulation. The porous bodies are particularly suitable for insulation at low temperatures since they suffer no substantial loss of elasticity even at very low temperatures, for example, the temperature of liquid air. It may be of advantage in this case previously to oxidize shaped insulating bodies superficially in order to prevent the penetration of moisture.

For electrotechnical purposes, the extremely low loss angle of the porous bodies produced according to the invention is of particular advantage. For this reason, materials of this kind can be used with great advantage in the production of cables of all kinds. Due to the very good heat-pressure resistance, they are particularly suitable for use as spacers for high-frequency cables.

The invention is illustrated in the following examples:—

EXAMPLE 1.

A mould prepared from sheet aluminium and having a width of 20 cm., a length of 30 cm. and a depth of 5.5 cm. was filled with 300 grams of pulverulent polyethylene having a particle size of less than 0.3 mm. the average molecular weight of the polyethylene being 300,000. After having carefully put on a cover which fitted into the mould and which was loaded with 16 kg., corresponding to a mechanical surface pressure of 26.7 gms./sq. cm., the mould was maintained in a heating cabinet for three hours at a temperature of 150° C. From the polyethylene which had

been charged in the pulverulent form, there was obtained a white porous plate which could readily be machined by cutting, sawing or drilling. The plate had a density of 0.27, a porosity of 75% and a thermal conductivity of =0.040, properties which correspond closely to the properties exhibited, for example, by cork.

EXAMPLE 2.

The mould used in Example 1 was employed with two charges (a) and (b), each of 500 grams, of polyethylene having a particle size of less than 0.3 mm. and an average molecular weight of 500,000. The cover of the mould with charge (a) was loaded with 26.7 gms./sq. cm. and with 3.3 gms./sq. cm. for charge (b). Both of the charges were placed for 2 hours in a heating cabinet maintained at 175° C. White porous plates were obtained in both cases. The plate from charge (a) had a thickness of 1.8 cm. and that from charge (b) a thickness of 3 cm. Both of the plates could be machined by cutting, sawing or drilling. The plate produced from charge (a) would, moreover, readily be machined on a lathe.

The plates had the following densities, porosities, and thermal conductivities:—

Charge	Load	Density	Porosity	Thermal Conductivity
(a)	26.7 gms./sq. cm.	0.54	45%	0.095
(b)	3.3 gms./sq. cm.	0.33	67%	0.048

EXAMPLE 3.

Glass cylinders of 35 mm. internal diameter and 200 mm. length were each filled with 25 grams of the same batch of polyethylene as that used in Example 1 and which had previously been freed extensively from air by repeated evacuation with the addition of nitrogen. A cylindrical piece of iron of a weight of 200 grams, corresponding to a load of 21 gms./sq. cm., was placed on the surface of the pulverulent polyethylene in each of the cylinders. The glass cylinders were placed in an oil bath which was maintained at the temperature desired. The polyethylene charges were maintained in a nitrogen atmosphere for the entire duration of the treatment in the bath.

The properties of the porous cylindrical bodies obtained at different temperatures are summarized in the following table:—

Temperature °C.	Duration of test Hrs.	Density	Porosity	Thermal Conductivity
200	1.5	0.58	40%	0.110
225	1.5	0.60	38%	0.115
250	1.5	0.63	35%	0.118
275	1.5	0.65	33%	0.122
300	1.5	0.66	32%	0.142

EXAMPLE 4.

25 grams of polyethylene of an average molecular weight of 300,000 and having a particle size of above 1 mm. were maintained for 1.5 hours at 150° C. under a load of 21 grams/sq. cm. in a glass cylinder having the dimensions set forth in Example 3. The porous cylindrical body obtained had a density of 0.44, a porosity of 55% and a thermal conductivity of =0.071.

EXAMPLE 5.

A cylindrical porous body which had been produced by treating polyethylene having an average molecular weight of 300,000 and a particle size of below 0.3 mm. for 1.5 hours at 175° C. under a load of 21 gms./sq. cm. was superficially melted with a hot air stream of 230° C. This resulted in the development of a glassy, continuous surface on the cylindrical body. The cylindrical body was afterwards immersed in water for 24 hours; no increase in the weight of the body occurred during this treatment.

What we claim is:—

1. A process for the production of porous polyethylene, which comprises subjecting small particles of polyethylene of a molecular weight greater than 75000 to heating at a temperature which is not less than 120° C. and which is below that temperature at which decomposition and/or gelation of the polyethylene occurs.

2. A process for the production of a body of porous polyethylene, which comprises heating, with or without the simultaneous application of mechanical pressure, a quantity of particulate polyethylene having a molecular weight greater than 75000 to a temperature between 120° C. and that temperature at which, under the conditions of pressure employed, decomposition and/or gelation of the polyethylene occurs.

3. A process according to Claim 1 or Claim 2, in which the polyethylene is of a molecular weight greater than 100,000.

4. A process according to any one of the preceding claims, in which another highly polymerised material is admixed with the polyethylene prior to the heating.

5. A process according to Claim 4, in which the other highly polymerised material is one or more of the members of the class comprising polystyrene, polyisobutylene and low molecular weight polyethylene.

6. A process according to any one of the preceding claims, in which the polyethylene is largely or wholly in pulverulent form.

7. A process according to any one of Claims 1 to 5, in which the particles of polyethylene or of the polyethylene-containing mixture are in the form of granules, fibres, scales, flakes, rings, discs, wire sections, tube sections, plate sections or small polyhedrons or mixtures thereof.

8. A process according to any one of the preceding claims, in which the polyethylene or the polyethylene-containing mixture contains or is in admixture with a dye and/or a filler.

9. A process according to any one of the preceding claims, in which the heating is effected in the absence of air or oxygen.

10. A process according to any one of the preceding claims, in which the heating is effected under vacuum.

11. A process according to any one of Claims 1 to 9, in which the heating is effected in an atmosphere of an inert gas, such as nitrogen or carbon dioxide.

12. A process according to any one of the preceding claims, in which, without the use of external mechanical pressure or at only moderate pressure, the temperature employed is below about 400° C.

13. A process according to any one of the preceding claims, in which, when a porous body having cork-like properties is to be obtained, the temperature employed is from 130° C. to approximately 170° C. with no external pressure or with only moderate pressure.

14. A process according to any one of the preceding claims, in which the heating is continued until the porous product attains the particular mechanical strength desired.

15. A process according to any one of the preceding claims, in which the heating is effected in two or more stages.

16. A process according to Claim 15, in which different temperatures and/or different pressures are used in two or more of the stages.

17. A process according to any one of the preceding claims, in which the supply of heat to the polyethylene or polyethylene-containing mixture to be processed is effected by means attached to the outside walls of the reaction vessels.

18. A process according to any one of Claims 1 to 16, in which the heating is effected, in whole or in part, by passing a preheated, inert gas or vapour through the polyethylene or polyethylene-containing mixture.

19. A process according to any one of Claims 1 to 16, in which the polyethylene is heated by means of a high-frequency electromagnetic field, the polyethylene being in admixture with a high polymer or a filler having a dielectric loss which is adequate to permit the polyethylene to be brought to the requisite temperature by such means.

20. A process according to any one of the preceding claims, in which the heating of the polyethylene or polyethylene-containing mixture is effected in a mould or like vessel whereby the porous product is obtained in a desired shape.

21. A process according to any one of the preceding claims, in which the surface of the porous product is rendered impermeable or made more impermeable by partial oxidation.

22. A process according to Claim 21, in which the partial oxidation is effected in a current of air at a temperature in the range 170°—200° C.

23. A process for the production of a porous body or mass comprising polyethylene, substantially as hereinbefore described.

24. A process for the production of a porous body or mass comprising polyethylene, substantially as hereinbefore described with reference to any one of the examples.

25. A process according to any one of the preceding claims, in which the polyethylene has been obtained by the polymerisation of ethylene at a temperature not substantially in excess of 100° C. and at a pressure below 200 kg./sq. cm.

26. A process according to Claim 25, in which the polymerisation is effected at a temperature in the range 20°—100° C.

27. An article comprising porous material produced according to the process claimed in any one of the preceding claims.

28. An article according to Claim 27, the density of the porous material being less than the density of water.

29. A spacer or other insulation member for use in a cable, particularly a high frequency cable, comprising the product obtained by the process claimed in any one of Claims 1 to 26.

30. Heat or sound insulation means, comprising the product, in granular or other form obtained by the process claimed in any one of Claims 1 to 26.

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